CHARACTERIZATION OF VISCOELASTIC PROPERTIES OF POLYMERIC MATERIALS THROUGH NANOINDENTATION

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ABSTRACT

Nanoindentation is used to determine the dynamic viscoelastic properties of six polymer materials. It is shown that varying the harmonic frequency of the nanoindentation does not have any significant effect on the measured storage and loss moduli of the polymers. Agreement is found between these results and data from DMA testing of the same materials. Varying the harmonic amplitude of the nanoindentation does not have a significant effect on the measured properties of the high-performance resins, however, the storage modulus of the polyethylene decreases as the harmonic amplitude increases. Measured storage and loss moduli are also shown to depend on the density of the polyethylene.

INTRODUCTION

Nanoindentation is a promising method of measuring the mechanical properties of materials at smaller length and load scales than allowed by other testing methods, thus allowing individual constituents and local regions of heterogeneous materials to be characterized individually. The ability to measure properties on the nanometer length scale is particularly important for the development of polymer composite materials in which the localized material structure can have a significant impact on the overall or bulk behavior. The basic methods for measuring elastic stiffness and strength properties [1] and quasi-static viscoelastic properties [2-5] of polymers through nanoindentation have been developed, however, the dynamic viscoelastic characterization of polymer materials through nanoindentation has not been studied in detail [6]. For time-dependent behavior, dynamic viscoelastic testing offers the advantage of significantly decreased testing time by examining properties over a range of frequencies rather than extended time. Consistent and accurate methods for obtaining the dynamic viscoelastic properties of polymers and their composites need to be established in order to facilitate the use and development of these materials.

The objective of the current paper is to establish experimental methods for dynamic nanoindentation and to investigate the ability of these nanoindentation methods to determine the dynamic viscoelastic response of bulk polymer materials. To accomplish these objectives, a series of nanoindentation tests were performed on six polymer systems, including two high-performance resins intended for elevated-temperature conditions, and four resins of high-density polyethylene (HDPE). The dynamic nanoindentation tests were conducted using a range of harmonic amplitudes and harmonic frequencies. Results from these tests, in the form of storage and loss modulus, are quantified and compared. The measured data is also compared with results obtained from standard Dynamical Mechanical Analysis (DMA) test data for the same polymer resins tested under similar conditions.

MATERIALS AND SPECIMENS

In this study, six polymer materials were used for viscoelastic characterization. The first material, designated 5260, is a modified bismaleimide polymer manufactured by BASF Corp. The second material, designated 8320, is a thermoplastic polymer manufactured by Amoco. The remaining four materials were high-density polyethylene (HDPE) at four different densities: 0.946, 0.947, 0.952, and 0.962 g/cc; and were manufactured by Aldrich Corp. in pellet form. All six of the materials were tested in solid form with the HDPE test specimens cut from plaques that were fabricated from the pellets via mold-press at NASA Langley Research Center.

For the nanoindentation specimens, small coupons were cut from the test materials with approximate dimensions 10 mm × 10 mm with a thickness at least or greater than 3 mm. The specimens were mounted onto the nanoindentation fixture using a Cyanoacrylate-based adhesive. A Buehler polishing wheel and 3 μm alumina polishing solution were used to prepare the testing surface of each nanoindentation specimen. Three DMA test specimens, per material type, were also cut with approximate dimensions of 50 mm × 12 mm and a thickness equal nanoindenter test specimen thickness.

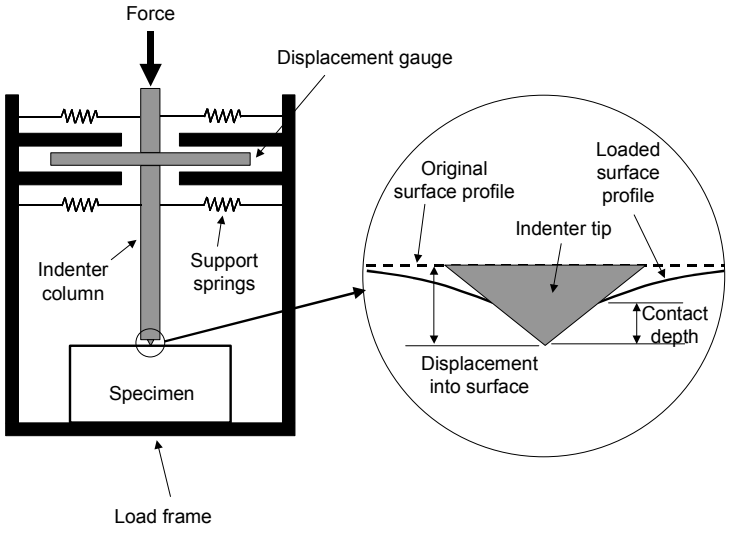

Fig. 1. Diagram of nanoindentation system

DYNAMIC NANOINDENTATION TESTING

The nanoindentation tests were performed with a MTS Nano Indenter® DCM (Dynamic Contact Module) system with a Berkovich indenter tip. The DCM is designed for a relatively high resolution at small loads and displacements, which is ideal for determining viscoelastic properties of polymers. A schematic of the nanoindentation system and indentation process is shown in Fig. 1. Referring to Fig. 1, a force is applied onto the indenter column, which drives the indenter head into the material. The displacement of the indenter column is continuously monitored. The Continuous Stiffness Measurement (CSM) method was used, which allows for a continuous measure of the stiffness of the material throughout the loading process by using a low magnitude oscillating force superimposed onto the overall quasi-static force signal. The displacement response is measured at the same frequency as the applied oscillating force and any resulting phase lag can be related to the dynamic stiffness of the material.

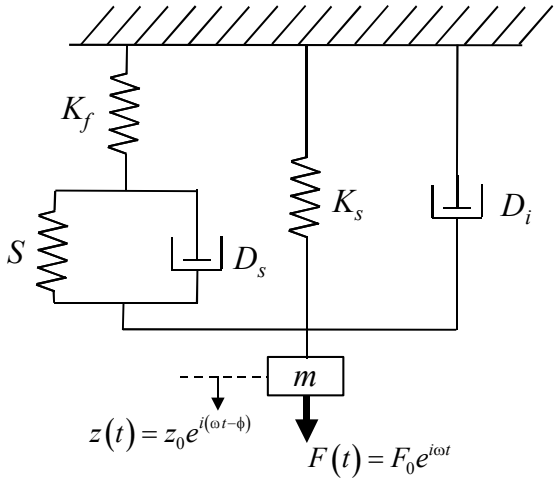

Fig.2. Mechanical model for nanoindentation

The apparatus shown in Fig. 1 can be modeled as shown in Fig. 2. The values of the support spring stiffness, K_s, the load frame stiffness, K_f, the indenter damping, D_i, and the indenter mass, m, are known *a priori*. The stiffness and damping of contact, S and D_s, respectively, depend on the materials and conditions at the contacting surfaces. The overall response of the system can be used to determine these parameters, which are subsequently used to determine the viscoelastic properties of the tested material.

If it is assumed that K_f provides the major contribution to the total stiffness such that K_f approaches ∞, then the force balance on the model shown in Fig. 2, in the contact direction, z, is given by

$$F\left(t\right) = m\ddot{z}\left(t\right) + \left(D_i + D_s\right)\dot{z}\left(t\right) + \left(K_s + S\right)z\left(t\right) \tag{1}$$

The driving or oscillating force is

$$F\left(t\right) = F_0 e^{i\omega t} \tag{2}$$

where F_0 is the force amplitude and ω is the harmonic frequency. The assumed particular solution for the displacement is

$$z\left(t\right) = z_0 e^{i\left(\omega t - \phi\right)} \tag{3}$$

where z_0 is the displacement amplitude and ϕ is the phase angle between the applied force and resultant displacement. Substitution of Eqs. (2) and (3) into (1) and simplifying yields

$$\frac{F\left(t\right)}{z\left(t\right)} = A_1 + iA_2 \tag{4}$$

and

$$\frac{F_0}{z_0} = \left(A_1\cos\phi + A_2\sin\phi\right) + i\left(A_2\cos\phi - A_1\sin\phi\right) \tag{5}$$

where the constants A_1 and A_2 are

$$\begin{aligned} A_1 &= K_s + S - m\omega^2 \\ A_2 &= \left(D_i + D_s\right)\omega \end{aligned} \tag{6}$$

The phase angle is

$$\tan\phi = \frac{\mathrm{Im}\left(F\left(t\right)/z\left(t\right)\right)}{\mathrm{Re}\left(F\left(t\right)/z\left(t\right)\right)} \tag{7}$$

The magnitude of the ratio of the force and displacement amplitudes is

$$\left|\frac{F_0}{z_0}\right| = \sqrt{\left[\mathrm{Re}\left(F_0/z_0\right)\right]^2 + \left[\mathrm{Im}\left(F_0/z_0\right)\right]^2} \tag{8}$$

Substitution of Eqs. (4), (5), and (6) into Eqs. (7) and (8), and solving simultaneously yields

$$S = \left|\frac{F_0}{z_0}\right|\cos\phi + m\omega^2 - K_s \tag{9}$$

and

$$\omega D_S = \left| \frac{F_0}{z_0} \right| \sin \phi - \omega D_i \tag{10}$$

The force and displacement amplitudes and the harmonic frequency of the applied force oscillations are measured by the nanoindentation system. The quantities in Eqs. (9) and (10) are subsequently used to determine the elastic and viscous components of the material behavior.

At a given frequency, the dynamic or oscillatory force, such as given in equation (2), will cause an oscillatory strain response at the same frequency but lagging behind by the phase angle, ϕ [7]. For viscoelastic materials, it is often convenient to express the overall constitutive behavior in terms of the complex modulus given by

$$E = E' + iE'' \tag{11}$$

where the storage modulus, E', is in phase with the strain and characteristic of elasticity, and the loss modulus, E'', is characteristic of internal damping. The storage modulus of the polymer determined through nanoindentation is [8]

$$E' = \frac{S}{2\beta} \sqrt{\frac{\pi}{A}} \tag{12}$$

where β is a constant that depends on the geometry of the indenter (β = 1.034 for the Berkovich indenter that is used in the present study) and A is the projected contact area. The projected contact area is determined as a function of contact depth (Fig. 1) using an empirical function which is established by indenting a material with a known modulus, as outlined by Oliver and Pharr [1]. Similarly, the loss modulus is [8]

$$E'' = \frac{\omega D_S}{2\beta} \sqrt{\frac{\pi}{A}} \tag{13}$$

where ωD_s is given by Eq. (10).

DYNAMIC MECHANICAL ANALYSIS TESTING

For comparison to the dynamic nanoindentation test results, Dynamic Mechanical Analysis (DMA) tests were performed on all the materials. The DMA tests are standard tests conducted using well-established procedures. Briefly, in DMA testing, an oscillatory force (in bending mode) is applied onto a bulk sample and the resultant dynamic modulus is measured. The test equipment allows for testing at multiple frequencies and the analysis of the data is similar to that outlined in the previous section. A complete description of this test method may be found elsewhere [9, 10].

CONTACT AREA CALIBRATION

For high stiffness materials such as thin film metallics, the projected contact area, A (Eqs. (12) and (13)), is determined by using a fused silica calibration standard. Because of the relatively low moduli of the test polymers with respect to the fused silica, the projected contact area was instead determined using the 5260 material as a calibration standard. Prior to determining the contact area, the Young's modulus of the 5260 at room temperature was measured using a strain-controlled tension test of an 8" × 0.5" × 0.14" specimen on a 2 kip servo-hydraulic test stand. A uniaxial strain gage was used to monitor the strain of the specimen and stress was calculated based on the measured load and the specimen's cross-sectional area prior to test. The response of the specimen was linear-elastic up to the point of failure (51 MPa). The measured Young's modulus was 4.3 GPa. Twenty-five indentations were made onto the 5260 nanoindentation specimen and the contact area was then subsequently determined as a function of contact depth by using Eq. (12), a fifth-order polynomial curve fit relating the tip area to contact depth, and the known Young's modulus of the tested material. The procedure is similar to that discussed elsewhere [1, 2].

TESTING PROCEDURES

The baseline procedure for the nanoindentation tests was to load at a strain rate of 0.05 s^{-1}, a harmonic frequency of 75 Hz, and a harmonic amplitude of 1 nm. All tests were conducted at room temperature. The storage and loss moduli were calculated for a depth range of 500 to 1400 nm. Up to 15 indentations were performed for every data point.

To study the effect of harmonic amplitude on the storage and loss moduli, a set of indentations were performed on each material in which the harmonic amplitude was varied from the baseline (1 nm) to 50 nm, while all other parameters remained unchanged. Similarly, the harmonic frequency was varied from 5 Hz to 115 Hz with the other parameters kept constant to examine its effect on the measured viscoelastic properties. To facilitate a direct comparison in measured response, the same materials were also tested with the DMA, at room temperature, at frequencies in the same range (5 to 115 Hz) and with a harmonic amplitude of 15 μm.

RESULTS, NANOINDENTATION AND DMA

Results from the nanoindentation and DMA tests are presented (Figs. 3-6) in terms of storage and loss modulus as a function of test variables or material type. On all plots, the error bars at specific data points represent the standard deviation as measured through repeat tests.

Typical storage and loss moduli for the 8320, 5260 and HDPE (density = 0.962 g/cc) are shown in Fig. 3 over the entire depth range tested at a harmonic amplitude and frequency of 10 nm and 75 Hz, respectively. The differences in elastic stiffness between material types are evident by the relative location of the storage modulus curves. For all materials, surface penetration of 200 to 400 nm was required before the storage modulus obtained a relatively constant value. The loss moduli for all material systems were nearly constant over the tested depth range.

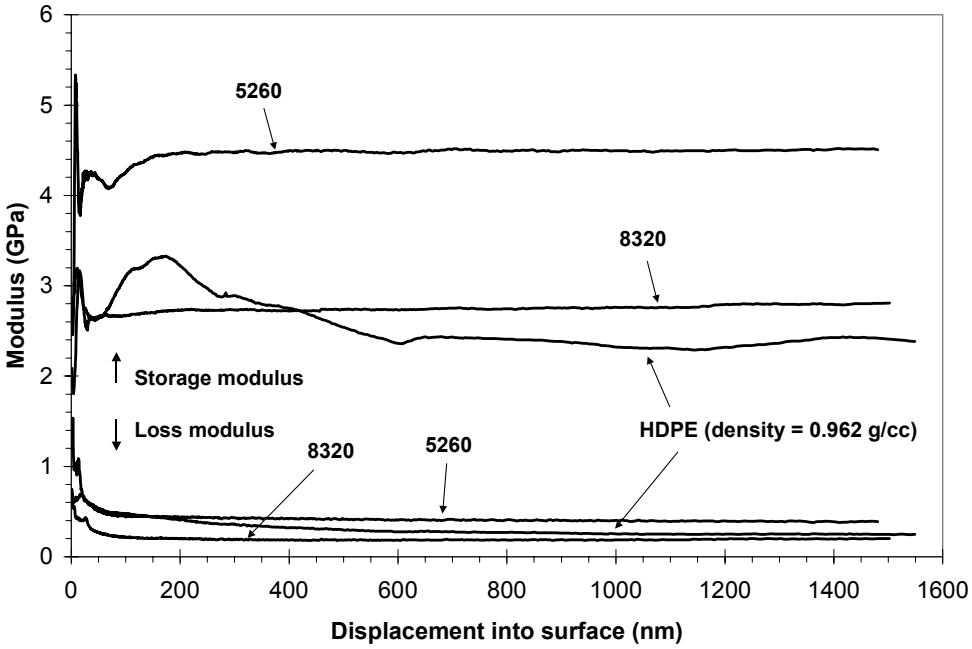

Fig. 3. Storage and loss moduli vs. displacement into surface for nanoindentation tests

From the nanoindentation tests, the measured storage and loss moduli for a range of harmonic amplitudes are shown in Fig. 4 for the 5260, 8320, and HDPE (density = 0.962 g/cc). For the 5260 and 8320, there was no significant influence of the harmonic amplitude on the viscoelastic properties. For the HDPE, the storage modulus decreased as the amplitude increased while the loss modulus did not change significantly. The measured moduli for a range of harmonic frequencies for the same three materials are shown in Fig. 5. The harmonic frequency did not have a significant effect on the measured viscoelastic moduli of any of the three materials. For comparison purposes, the viscoelastic properties of these materials determined using the DMA is also shown in Fig. 5. In general, there was good agreement between the two test methods except for the case of the 8320 storage modulus that showed up to 30% difference between the methods.

From the nanoindentation tests, the storage and loss moduli for all four densities of HDPE are shown in Fig. 6 for various harmonic amplitudes. While the loss modulus was not significantly affected by either the harmonic amplitude or the density, the storage modulus increased with increasing density and decreasing harmonic amplitude. The data show reasonable agreement in trends with density for all three materials over the entire test range.

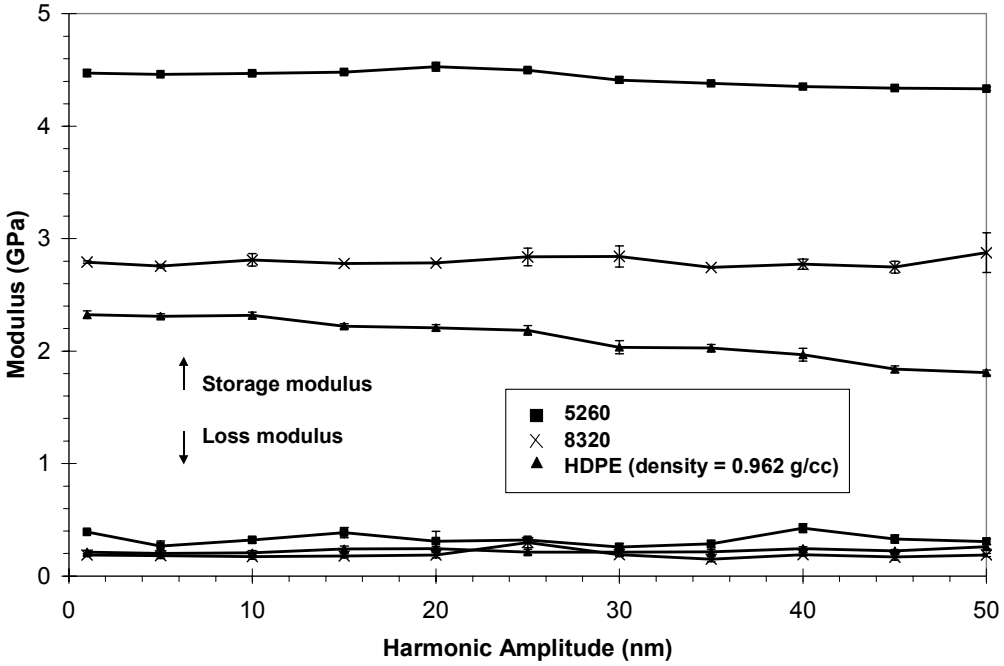

Fig. 4. Storage and loss moduli vs. harmonic amplitude for nanoindentation tests

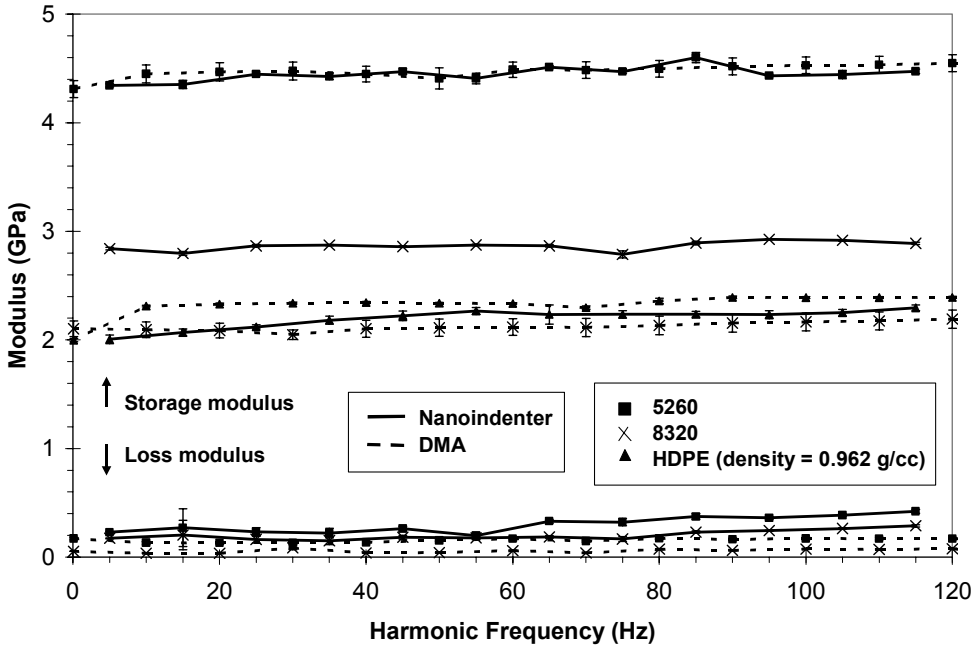

Fig. 5. Storage and loss moduli vs. harmonic frequency for both the nanoindenter and DMA test methods

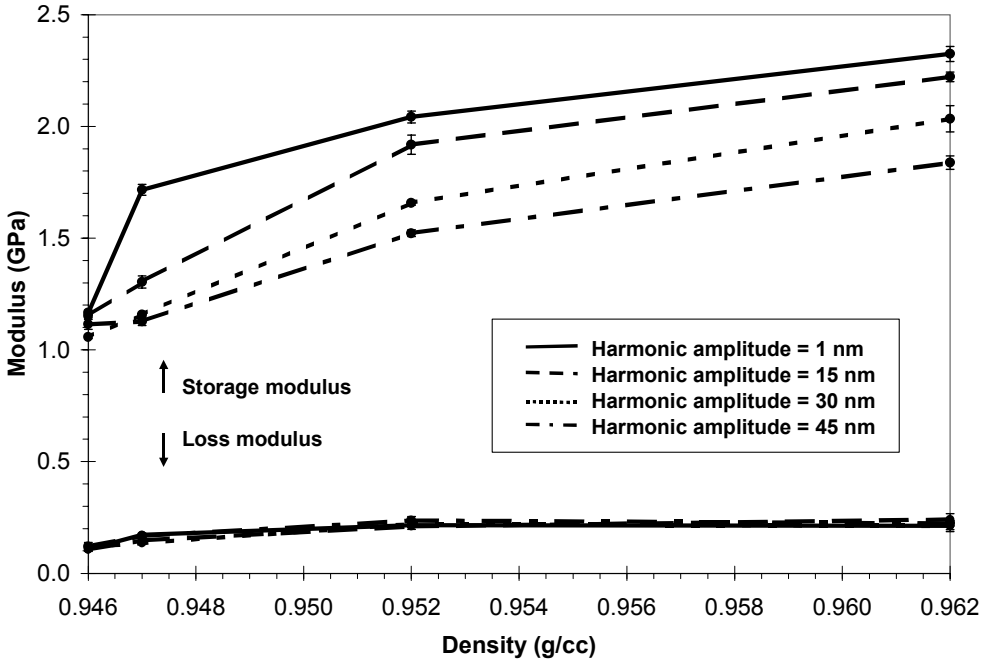

Fig. 6. Storage and loss moduli of HDPE vs. HDPE density for the nanoindenter tests

SUMMARY

In this study, the objective was to explore the ability of nanoindentation testing to determine the dynamic viscoelastic properties of polymer materials. Test variables included harmonic frequency and harmonic amplitude. Six polymers consisting of two high-performance materials (8320, 5260) and four density variations of polyethylene were tested by nanoindentation and the results were compared to standard DMA test results to verify the procedures. It was shown that varying the harmonic frequency of the nanoindentation did not have any significant effect on the measured storage and loss moduli of the polymers. Good agreement was found between these results and data from DMA testing of the same materials. Varying the harmonic amplitude of the nanoindentation did not have a significant effect on the measured properties of the high-performance polymers (8320, 5260), however, the storage modulus of the polyethylene material decreased as the harmonic amplitude increased. Measured storage and loss moduli were also shown to be sensitive to the density of the polyethylene.

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